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Removal of Ionic Copper Contamination from the Marine Environment

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13. ABSTRACT (*Maximum 200 words*)

A major source of trace metal contamination in the marine environment comes from the copper-containing anti-fouling coatings on ship hulls. In a shipyard, these hulls release ionic copper into confined spaces such as dry docks. The releases can come from the coatings on the hill, or the debris and waste fines produced in the hull cleaning operation. The unified national discharge standards (UNDS) will eventually restrict releases of ionic copper. Therefore, it is important to develop an inexpensive but useful technology to remove the ionic contaminant from the water. To make this removal possible, a technology based on absorption and recovery of the ionic copper is considered. A set of nine materials with trace metal absorption capability were investigated (cellulose, live plankton, dead plankton, live algae, chitin, zeolite, milled chitosan, flake chitosan, and algin). The analyses used flaked chitosan as the comparison base. It is assumed that flaked chitosan prepared from seafood waste chitin would be the most cost effective. In addition, there would be a cost in developing a filter system to clean the ionic copper containing waste, recycle the cleaned water, and recover the copper. The conclusions from this study are: (1) chitosan is a good absorber of ionic copper; (2) chitosan can be developed from seafood waste through a relatively simple chemical process; (3) chitosan can be used after recovery of the copper contamination; and (4) the process will not harm the marine environment.

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REMOVAL OF IONIC COPPER CONTAMINATION
FROM THE MARINE ENVIRONMENT

I. INTRODUCTION

In marine waters, copper can be present in a range of physiochemical forms that are either dissolved or incorporated into a particle (Table 1). When copper is dissolved it can be present as a hydrated ion, organic and inorganic complexes, and colloidal dispersions (Morrison et al 1989). Copper in its ionic state is often present as both the Cu(I) and Cu(II) valence state. Anti-fouling coatings containing copper leach Cu(I) which converts to Cu(II) (Figure 1). These ionic forms are toxic to fouling organisms.

Table 1.
Copper Toxicity and Electrochemical Lability
(Data derived from Morrison et al 1989)

COPPER SPECIES	TOXICITY TO A MARINE DIATOM	LABILITY
Cu(II) Ionic	HIGH	LABILE
CuCl^2 Ionic	HIGH	LABILE
CuCO$_3$ Complexed	LOW	INERT
Cu(EDTA^1) Complexed	LOW	INERT
Cu(Fulvate) Complexed	LOW	INERT
Cu(Humic Acid/FeO$_3$) Complexed	MEDIUM	QUASI-LABILE
Cu(DMP^2) Complexed	HIGH	INERT

1) Ethylenediaminetetraacetic acid
2) 2,9-Dimethyl-1,10-Phenanthroline

Table 1 demonstrates that ionic copper is both toxic and electrochemically labile. Aquatic organisms seem to be able to de-toxify copper by binding it to organic compounds like fulvic acid (Morrison et al 1989). This then is a measure of the complexation capacity of the marine water. Table 2 represents copper complexation by organic ligands. Note that fulvic acid, an ever present organic ligands in coastal runoff waters, has a high affinity for ionic copper.

Table 2.
Ionic Copper Complexation Capacity Derived from a Bioassay Test Using
Organic Ligands at a pH of 7.0 and a Salinity of 0.00.
(data from Morrison et al 1989).

SOURCE WATER	COMPLEXATION CAPACITY $(x10^{-6}M)$
Ethylenediaminetetraacetic Acid (10^6M)	1.04
Fulvic Acid @ 25 mgl^{-1}	17.5
Australian Streams and Reservoir	mean=3.3 (range=2.5 - 4.1)

Ionic copper distributes widely through the marine environment as shown in Figure 1. Because of copper's ability to react with various ligands in the water column it is a very difficult ion to measure and thus assess toxic capability once released from the anti-fouling coating. However, due to its initial toxic property, it is an important anti fouling chemical.
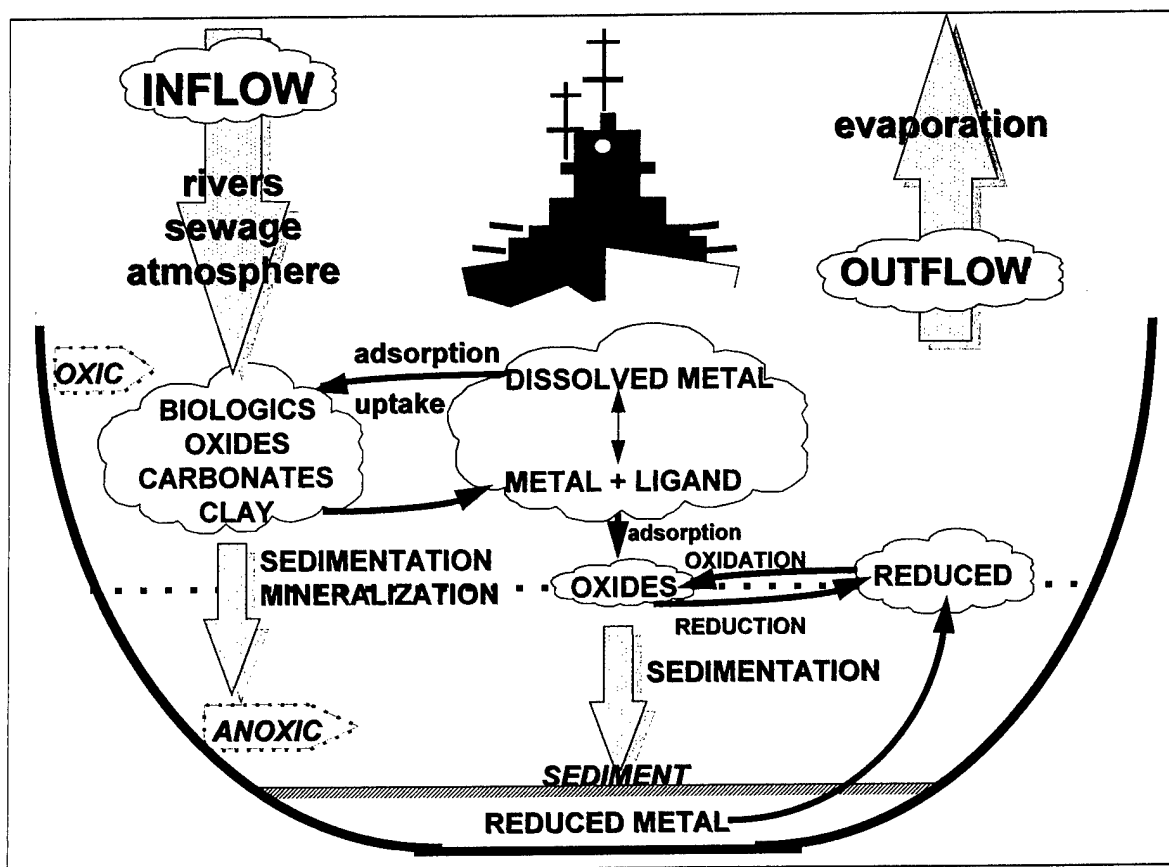

Figure 1. Pathways for movement of trace metals in general and copper in particular through the marine environment (adapted from Sigg 1994).

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The control of fouling is both an economic and operational problem associated with vessels deployed in the aquatic environment. Fouling processes roughen a vessel hull. This roughness in turn translates to increased drag which results in increasing fuel consumption to maintain operational requirements (Hare 1994; Claisse and Alzieu 1993; Wynne and Guard 1997). To ameliorate these costs and reduce demands on resources, anti-fouling coatings are used, and are the most effective in controlling fouling on vessel hulls (Hare 1994).

The anti-fouling coating contain toxins which slowly release into the stationary laminar water layer surrounding the moored hull. This layer provides an environment containing sufficient toxin to prevent free swimming larvae of fouling organisms from settling and attaching to the vessel hull. From the stationary laminar layer the toxin dissolves out into the surrounding water along a diffusional gradient (Hare 1994). The purpose of the anti-fouling coating is to maintain toxin concentrations in this stationary laminar layer high enough to prevent fouling. If leaching is too slow, the toxin concentration will be insufficient to prevent attachment of fouling species. If the leach rate is too great, the toxin in the anti-fouling coating will be rapidly exhausted. Rapid exhaustion will increase treatment costs, and shorten vessel in-service time.

Environmental factors, also, will affect both the fouler and the anti-fouling coating. Such factors as temperature, salinity, pH, and current flow will affect settlement of the fouler and the release of the toxin. For example, fouling is greater in the warm water of the tropics. Fouling is less if a vessel has a rapid turn around time and transit speeds of 4-5 knots are maintained (Hare 1994). Toxin release reduces 20% in copper containing anti-foulant coatings for each 0.1 increase in pH above a pH of 8.4. Toxin release increases by 25% if the pH drops below 8.0 (Hare 1994). Leaching of the toxin varies proportionally with the square of the salinity (Fletcher 1965). As the temperature increases one degree Celsius, leaching of the toxin will increase by 5% (Fletcher 1965). Thus a vessel traveling from temperate waters to tropical waters will have the effectiveness of the anti-fouling toxin increased. In addition, application and removal of ant-fouling coatings poses an environmental problem.

The removal processes creates fines (particles) containing the toxin (i.e. copper oxide) which can enter the local aquatic environment. These fines can create a toxin source. In addition, application and re-application of the anti-fouling coating can create a reservoir of toxin in the aquatic habitat through spills, over-spray, and mooring of freshly coated hulls. Within a harbor or dry dock facility, there is a potential for establishing contamination of aquatic resources which can continue of a long period of time (Figure 2). To help resolve the problem of the contaminated waste entering the local aquatic habitat, there is a need for a mechanism to contain and de-toxifying these releases. The following is a test of natural substances that could de-toxify the anti-fouling wastes.

The majority of navy ships use an anti-fouling coating containing copper. Now the Navy has a problem with trace metals produced during shipyard hull refurbishment (grinding and repainting a hull). At present, there is no simple method to reduce this contamination in a timely and cost effective manner. This work studied some relatively portable and cost effective methods for removing

this contamination. Since copper in its ionic state is very reactive chemically, it is possible to de-toxify the releases. These contaminants are subject to transformation and dispersal processes (Figure 3).
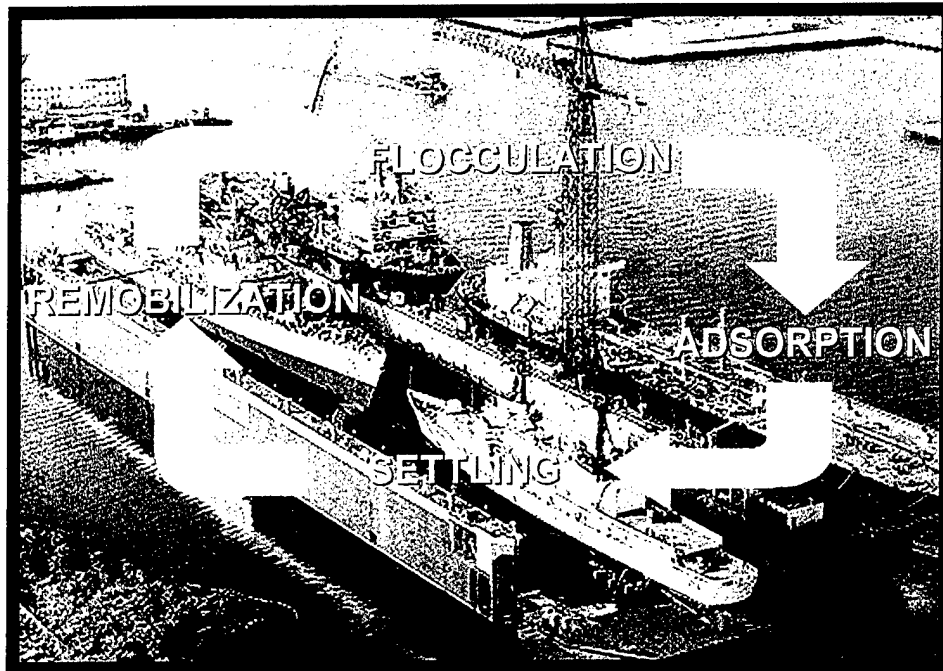

Figure 2. Cycle of ionic copper contamination in areas such as drydocks and harbors.

In this study, the test trace metal was ionic copper [Cu (I) and (II)]. Ionic copper is the primary contaminant released from ship hulls during the cleaning and re-coating process (Figure 4). Therefore, this study tests the hypothesis that the organic molecule poly-glucosamine (chitosan) is an appropriate trace metal absorbant to use in de-toxifing trace metal containing shipyard waste.
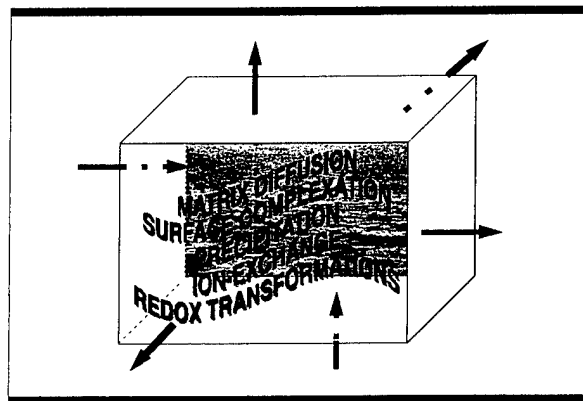
Figure 3. Important reactions that affect the ionic copper in the marine environment (redrawn from Bidoglio 1994).
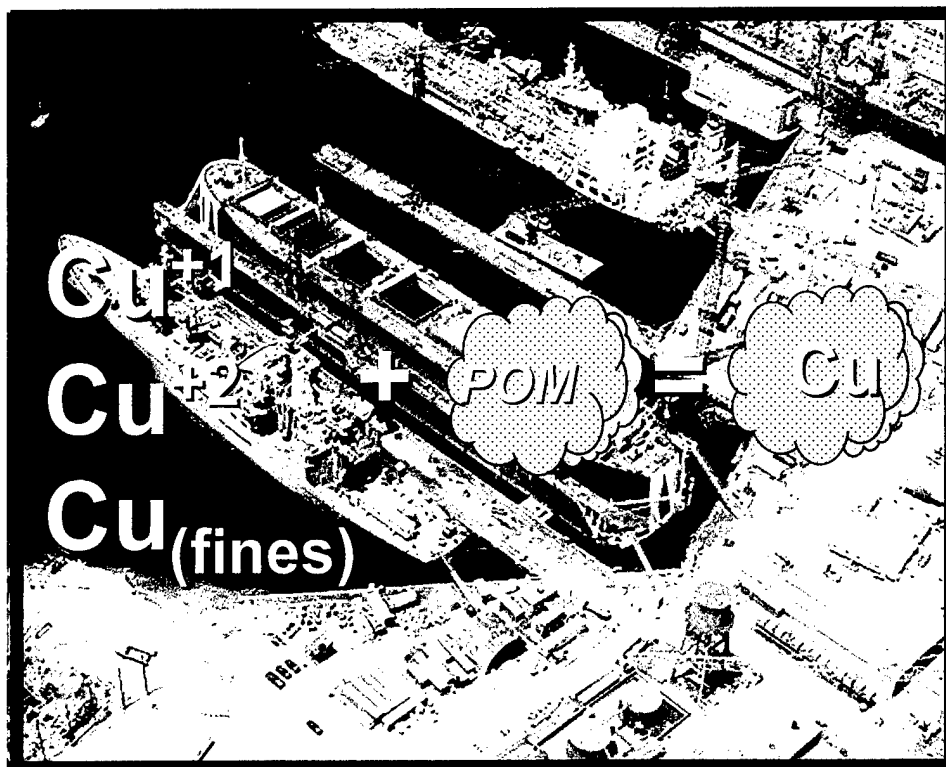
Figure 4. Reaction of ionic copper released from the antifouling coating and from the fines with particulate organic matter (POM). This creates a reservoir of copper that settles to the bottom in areas like dry docks and harbors.

The method studied takes advantage of a common seafood waste (shells from shrimp). This shell waste (Figure 5) is composed principally of chitin
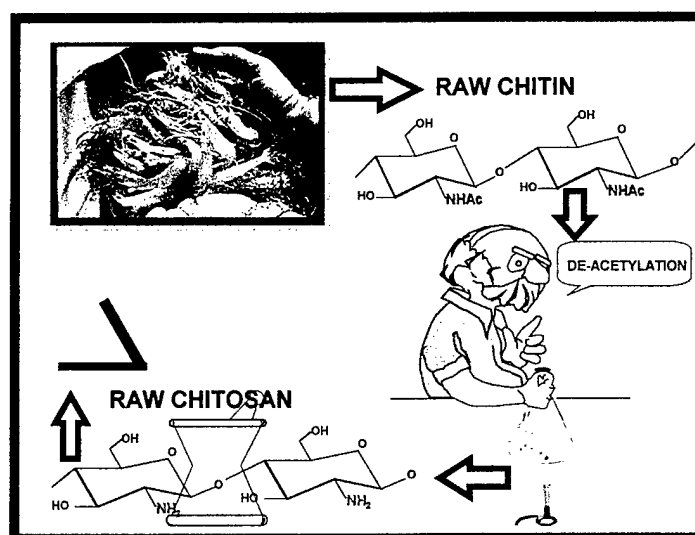

Figure 5. Summary of the process for preparing chitosan which can then be used to remove ionic copper

(*N*-acetyl-D-glucosamine). Chitin, when chemical processed, becomes chitosan [poly(D-glucosamine)] and is highly absorbant for trace metals. It has a strong metal chelating ability (Yang and Zall 1984, Guibal et al 1998).

II. MATERIALS AND METHODS

In this study, a series of tests were performed on various filtering media to test their absorption of ionic copper. The media tested were:
- cellulose (Millipore HAWG 0.45μ filter)
- live plankton (collected from Chesapeake bay)
- live algae (collected from a landscaping pond)
- zeolite
- reagent grade Chitosan (polyglucosamine)
- dead plankton (alcohol treated)
- raw Chitosan [poly(D-glucosamine)] (from shrimp shells)
- Chitin (from shrimp shells)
- Algin (calcium alginate)

All testing was done at 25°C using water having a salinity of either 0 or 35 parts per thousand (ppt). Filter media were rinsed in 250ml of distilled water prior to adding the ionic copper.

The 0 ppt water (pH=6.5) was made from distilled and reverse osmosis de-mineralized water. Seawater at 35 ppt (pH=7.6) was prepared from Instant Ocean salts added to the 0 ppt water. Both waters were tested for the presence of ionic copper using the Bathocuproine (BCP) method (Clesceri et al 1998). Measurements of Cu(II) concentrations were done with a Klett-Sumerson Colorimeter having # 48 green filter. Standard ionic copper solutions were prepared from SPEX reagent grade Cu(II) solution at a concentration of $1mgl^{-1}(1000\mu gl^{-1})$.

All filtration used a 250ml, chemically cleaned, glass filter bowl attached by a metal clamp to a sintered glass filter holder mounted in a rubber stopper on a 1L vacuum flask. Filtration was by vacuum using a Barnant vacuum pump adjusted to a vacuum pressure of 20 inches of mercury. Test samples were shaken for 120 minutes at 60rpm on a Labline platform, orbital shaker.

Filtering media were made as follows:

1. Cellulose - a 0.45μ porosity filter (Millipore HAWG 45mm) was used;

2. Live Plankton - collected from Chesapeake Bay by towing a #20 mesh plankton net. Samples of approximately 1g wet weight were prepared. An additional 1g sample was dried for 24 hours at 100°C then cooled and the dry weight measured. A relation between wet weight and dry weight was established so that the results could be calculated as mg of Cu(II) taken up by 1g of dry biological material. The wet weight samples were placed in 250ml of sample water containing 1mg of Cu(II). After 120 minutes, water was removed for copper analysis using the BCP method.

3. Live Algae - collected from a landscaping pond and placed in culture. The culturing was in the laboratory in water having $1mgl^{-1}$ of added nitrate and $100mgl^{-1}$ of added ortho-phosphate under continuous incandescent low light

levels at a temperature of 25°C. No attempt to establish axenic cultures (pure, bacteria free) was made. The only purpose was to develop biomass for the copper study. Samples of approximately 1g wet weight were prepared. An additional 1g sample was dried for 24 hours at 100°C then cooled and the dry weight measured. A relation between wet weight and dry weight was established so that the results could be calculated as mg of Cu(II) taken up by 1g of dry biological material. The wet weight samples were placed in 250ml of sample water containing 1mg of Cu(II). after 120 minutes, water was removed for copper analysis using the BCP method.

4. Zeolite - an absorbent clay material was weighed to make 1g samples. The samples were placed in 250ml of sample water containing 1mg of Cu(II). After 120 minutes, water was removed for copper analysis using the BCP method.

5. Reagent grade Chitosan [poly(D-glucosamine)] - reagent grade poly-glucosamine (Chitosan) was purchased from Aldrich Chemical Co. Samples having 1g of weight were prepared. The samples were placed in 250ml of sample water containing 1mg of Cu(II). After 120 minutes, water was removed for copper analysis using the BCP method.

6. Dead plankton - collected from Chesapeake Bay by towing a #20 mesh plankton net. The collected sample was treated with 70% isopropyl alcohol to stop all biological activity. Next, the sample was subjected to the following cleaning procedure:

- DEPROTEINATE IN DILUTE AQUEOUS NaOH
- RINSE IN DE-IONIZED WATER
- DECALCIFY WITH DILUTE AQUEOUS HCl
- RINSE IN DE-IONIZED WATER
- DECOLORIZE IN 0.5% $KMnO_4$ aq. AND AQUEOUS OXALIC ACID
- RINSE IN DE-IONIZED WATER
- DEACETYLATE IN HOT CONCENTRATED (40-50%) NaOH
    SOLUTION
- RINSE IN DE-IONIZED WATER
- EVACUATE TO DRY

Samples of approximately 1g wet weight were prepared. An additional 1g sample was dried for 24 hours at 100°C then cooled and the dry weight measured. A relation between wet weight and dry weight was established so that the results could be calculated as mg of Cu(II) taken up by 1g of dry biological material. The wet weight samples were placed in 250ml of sample water containing 1mg of Cu(II). After 120 minutes, water was removed for copper analysis using the BCP method.

7. Raw (flake) Chitosan - prepared from shrimp shells. The shells are coarse ground and chemically treated to produce chitosan [poly(D-glucosamine)], a polyglucosamine (modified after Findon et al 1993). The procedure is as follows (Figure 6):

- GRIND SHRIMP SHELLS INTO SMALL PIECES (use a blender);
- DEPROTEINATE IN DILUTE AQUEOUS NaOH;
- RINSE IN DE-IONIZED WATER;
- DECALCIFY WITH DILUTE AQUEOUS HCl;

- RINSE IN DE-IONIZED WATER;
- DECOLORIZE IN 0.5% KMnO$_4$ aq. AND AQUEOUS OXALIC ACID;
- RINSE IN DE-IONIZED WATER;
- DEACETYLATE IN HOT CONCENTRATED (40-50%) NaOH
        SOLUTION;
- RINSE IN DE-IONIZED WATER;
- REPEAT DEACETYLATION AND DE-IONIZED WATER RINSE:
- DRY

Samples having 1g of weight were prepared. The samples were placed in 250ml of sample water containing 1mg of Cu(II). After 120 minutes, water was removed for copper analysis using the BCP method.

8. Chitin - prepared from grinding shrimp shells. Samples having 1g of weight were prepared. The samples were placed in 250ml of sample water containing 1mg of Cu(II). After 120 minutes, water was removed for copper analysis using the BCP method.

9. Algin - Unmilled algin (calcium alginate) was obtained from the Kelco Co. in San Diego. This is a process extraction of the compound sodium alginate. Samples having 1g of weight were prepared. The samples were placed in 250ml of sample water containing 1mg of Cu(II). After 120 minutes, water was removed for copper analysis using the BCP method.
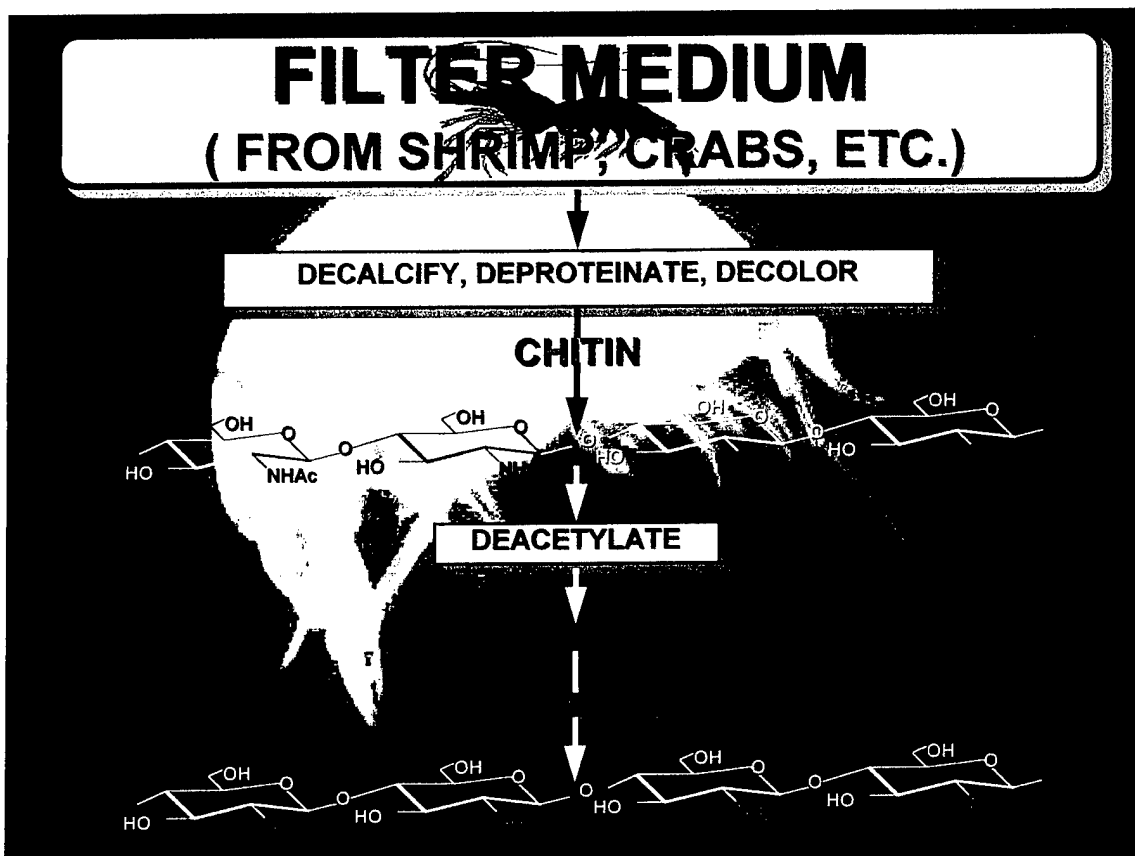
Figure 6. Making of Chitosan.

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The results obtained from all samples filtered through Millipore HAWG 45mm filters were corrected for Cu(II) absorption by the filter. After removal of the liquid from the test media, the media were subjected to chemical recovery. Recovery of Cu(II) was attempted by subjecting the media to dilute reagent grade acetic acid (2%), and distilled white vinegar. Chitosan absorbs trace metals and can be regenerated with a dilute aqueous acid (i.e. acetic acid). Chitosan tends to dissolve in strong acids (Ghandi 1997). This allows for cost effective recovery of the trace metals without costly landfill burial. The advantage is that the system is simple to use, re-usable, and provides water recycling.

III. RESULTS AND DISCUSSION

Ionic copper [Cu(I) and Cu(II)] posses a problem for aquatic biota (Sorensen 1991, Buffle et al 1990). Copper ion demonstrates that (Buffle et al 1990):

• the free ion activity of copper elicits a biological response and not the total metal concentration;

• the total copper metal partitions between dissolved, colloidal and particulate phases;

• the copper uptake by organisms is affected by the metal association with other compounds;

• the dynamics of the free ionic form of the copper varies with total loading and pH.

Thus, ionic copper complexation by dissolved and particulate complexers in marine waters will determine the buffering response, biological uptake and ecological transport. Pollutants such as ionic copper from anti-fouling coatings interact with the water and other chemicals present. This interaction includes precipitation, redox transformation, aqueous complexation, physical and chemical adsorption, biological transformations and colloid filtration (Bidoglio 1994, Figure 3).

Table 3
Abiotic environmental affects on ionic copper (data from Sadiq 1992)

FACTOR (INCREASING)	RELATIVE TOXICITY
SALINITY	DECREASE
CARBONATE	DECREASE
COMPLEXATION	DECREASE
ZINC	INCREASE
WATER SOLUBLE LIGAND	DECREASE
LIPID SOLUBLE LIGAND	INCREASE
TEMPERATURE	INCREASE

In sea water, trace metals like ionic copper coming from anti-fouling coatings can exist as a variety of chemical species. This influences their availability to both targeted and non-targeted organisms. Copper exists as a cation that is complexed by inorganic and organic ligands, adsorbed or bound within particles (Sunda 1994). Copper can cycle between different oxidation states thus affecting its behavior. Table 3 summarizes some of the abiotic affects of the environment on the toxicity of ionic copper. Therefore, it is important to reduce possible toxic ionic copper levels in the marine environment.

III-A. Test Media

This work looks at seven chemical and biological compounds that can actively complex and render the ionic copper relatively non-available to the marine biota. In addition, the complexed ionic copper is subjected to a recovery procedure.

The overall results of the compounds tested are in Figure 7. Testing criteria included an ability to complex ionic copper and to be regenerable. Regeneration would allow the complexing agent to be re-used, the ionic copper to be recovered and a reduction in potential landfill waste. A description of each of the compounds follows. Algin is not reported because it forms a gel when added to the test water, and no water is left to analyze for remaining copper. In all the experiments, a 10% solution of acetic acid and undiluted white distilled vinegar were used for regeneration.
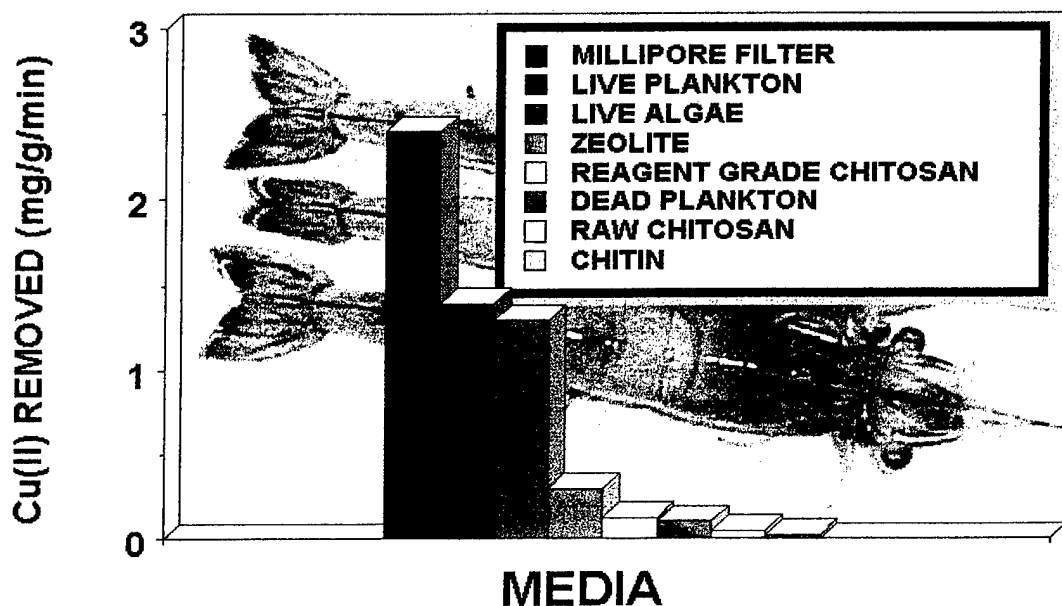

Figure 7. Comparison of the speed of uptake by the various media tested.

In all the following analyses, the compounds are compared to raw chitosan.

1. MILLIPORE FILTER. The Millipore filter is made from cellulose and is very adsorbent to metal ions. Figure 8 compares the commercially manufactured cellulose filter (Millipore HAWG45) to raw chitosan. However, cost of the processed cellulose and its resistance to regeneration by acetic acid and vinegar makes it a difficult compound to use. Recovery from cellulose might be possible through incineration.
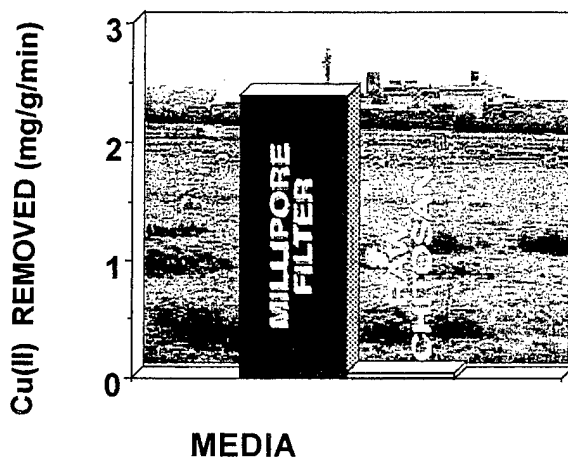

MEDIA

Figure 8. Comparison of absorption of Cu(II) by commercial cellulose to raw chitosan.

2. LIVE PLANKTON. The experiments with live plankton confirm the literature reports (Slauenwhite and Wangersky 1991, Volesky and Holan 1995, Moffett et al 1997) that live biomass absorbs trace metals. Sunda 1994 has shown how marine phytoplankton respond to trace metals (Figure 9). A comparison of live plankton to raw chitosan (Figure 10) shows a quicker "de-toxification" of the Cu(II) than raw chitosan. Figure 11 represents the increased ability of live plankton to absorb ionic copper when compared to dead plankton. However, plankton culturing, and concentration processes are time consuming, thus adding a layer of cost and time on detoxifying ionic copper and recovering the media.

3. LIVE ALGAE. The experiments with live algae grown from water in a landscaping pond confirm the literature reports (Moffett et al 1997) that live algal biomass absorbs trace metals. A comparison of this live algal biomass to raw chitosan (Figure 12) shows a quicker "de-toxification" of the Cu(II) than raw chitosan. However, the culturing, and recovery processes are time consuming. This adds an additional layer of cost and time to processing and recovery.

4. ZEOLITE. Figure 13 is a comparison of the absorption of Cu(II) by the compound, Zeolite, to raw chitosan. Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminum, silicon, and oxygen in their regular framework. Cations and water are located in the pores. Zeolite is effective in removing Cu(II) but further testing shows the Cu(II) to be held and not easily recovered by dilute acid treatment. Zeolites are best

Zeolites are best regenerated using ion exchange with sodium to remove cations. This adds an additional treatment layer and expense beyond that of acid/base recovery. As a single treatment compound, it appears to work well but creates a disposal problem.

5. REAGENT GRADE CHITOSAN. Chitosan [poly(D-glucosamine)] obtained from the Aldrich Chemical Company was tested (Figure 14). This is a milled product and when added to the water containing Cu(II) formed a gel. Treatment with acetic acid and vinegar did not release the complexed Cu(II) ions. Once the gel formed it was difficult to move water through it and it clogged the testing equipment.
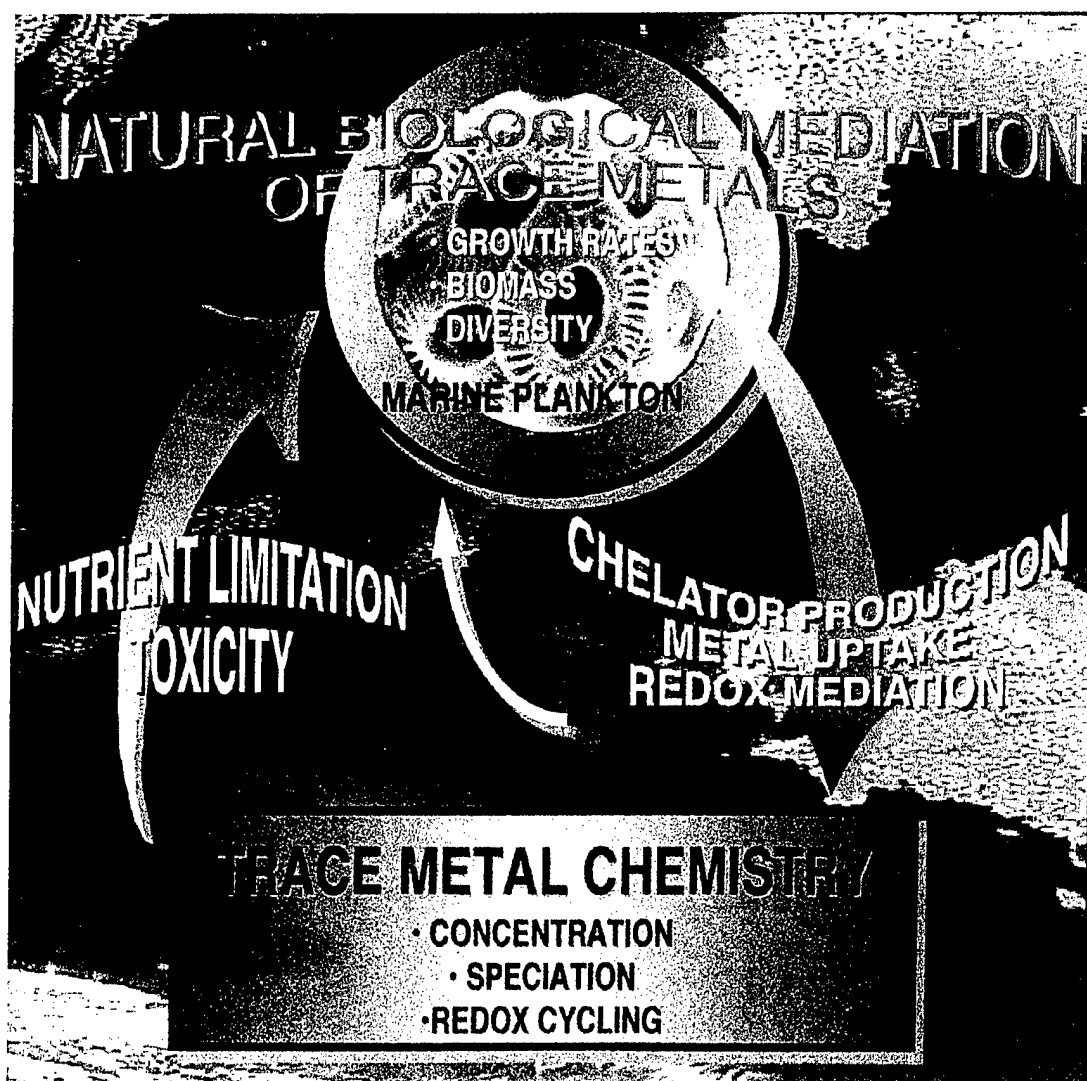
Figure 9. Example of a plankton bloom overlain with the influence of trace metals on marine plankton and the effect of the plankton on trace metal chemistry (re-drawn from Sunda 1994).
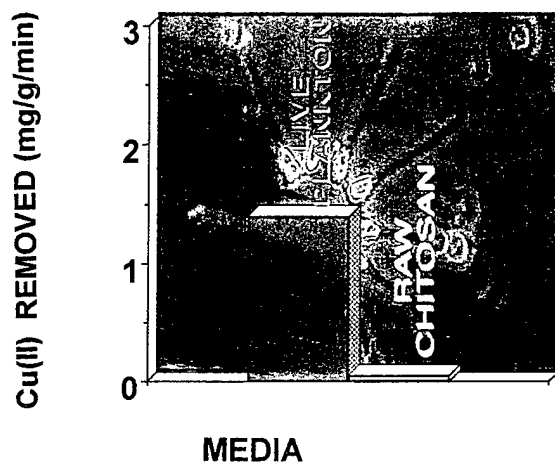
Figure 10. Comparison of the uptake of Cu(II) by live plankton collected from the Chesapeake Bay with raw chitosan.
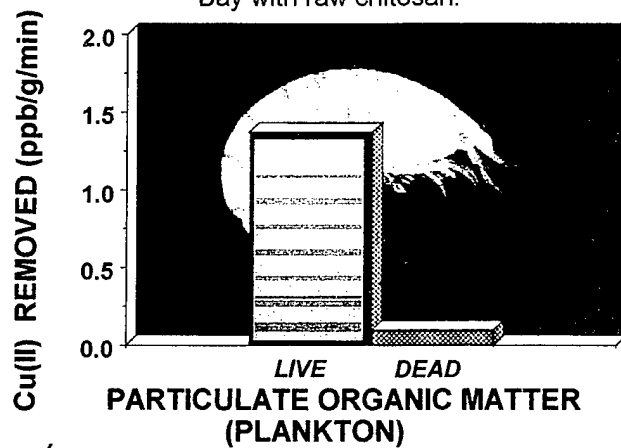
Figure 11. Comparison of the uptake of Cu(II) by live plankton and dead plankton collected from the Chesapeake Bay.
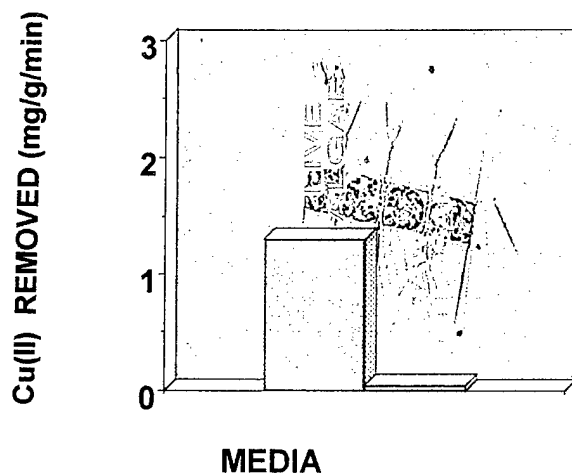

Figure 12. Comparison of the uptake of Cu(II) by live algae collected from a landscaping pond with raw chitosan.
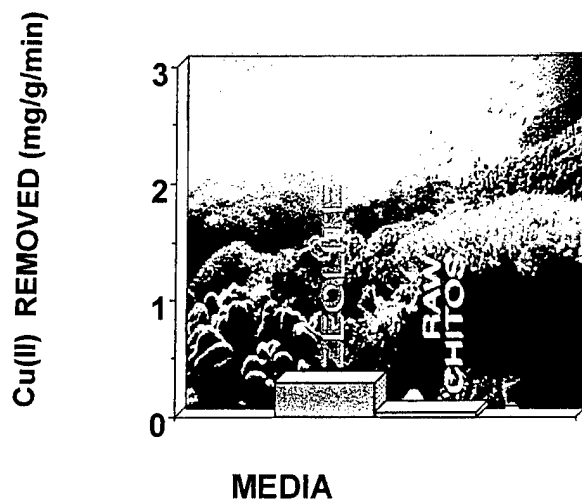
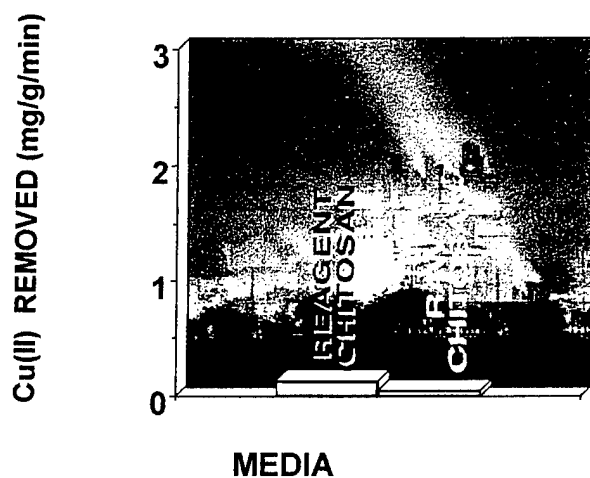**Figure 13.** Comparison of the uptake of Cu(II) by the clay compound Zeolite with raw chitosan.

Figure 14. Comparison of the uptake of Cu(II) by the reagent grade, milled chitosan with raw chitosan.

6. DEAD PLANKTON. Alcohol preserved plankton was tested for its ability to absorb Cu(II). The dead plankton were a simulation of organic ligands present in the water (Figure 15). As with the live plankton, a source is needed. This means that culturing, and recovery processes are needed. These processes are time consuming and add an additional layer of cost to processing and recovery.

7. CHITIN. The raw material that is used to make chitosan, chitin (N-acetyl-D-glucosamine), was tested. It was cleaned and rinsed prior to adding Cu(II). A small amount of Cu(II) appeared to be absorbed (Figure 16).

The compound algin, obtained from Kelco, Inc. of San Diego CA was tested. Upon adding water, it immediately gelled forming a semi-solid mass that was difficult to work with and regenerate.
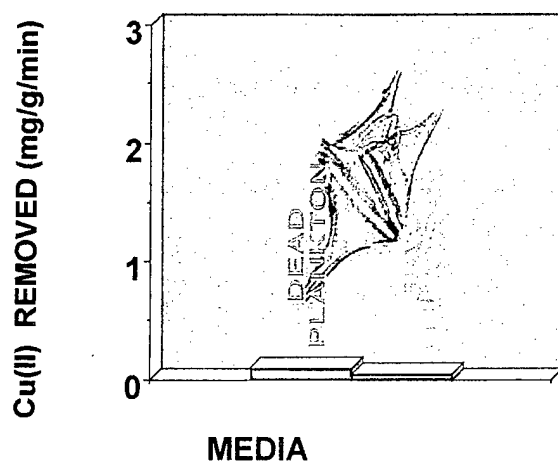
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Figure 15. Comparison of the uptake of Cu(II) by dead plankton with raw chitosan.
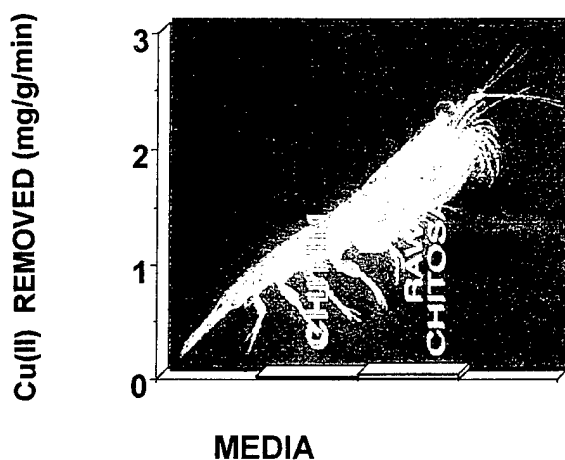

Figure 16. Comparison of the uptake of Cu(II) by chitin from shrimp shells with raw chitosan.

8. CHITOSAN. Of all the compounds tested, raw, un-milled chitosan appeared to offer the best all around absorbent for ionic copper. The raw chitosan could be regenerated and re-used. This allowed recovery of the copper and reduced further contamination and landfill problems. Ionic copper mobilized and released into the environment, whether from the anti-fouling coatings of a ship hull or from the waste produced in hull cleaning, tend to persist. Effective removal of the ionic copper can only occur when it is both immobilized and concentrated (Volesky and Holan 1995). This concentration must reach a point where it is economical to recover the complexed copper. The compounds tested here allow the ionic copper to be concentrated, and in some instances recovered. Findon et al (1993) report that the absorption of ionic copper is in the region of 40mg of ionic copper per gram of chitosan.

Chitosan prepared from waste shells of shrimp and crabs is a natural polysaccharide that has a high nitrogen content (Findon et al 1993, Guibal et al 1998). This helps the polysaccharide to absorb more trace metals (Muzarelli

1971, Hauer 1978, Findon et al 1993). In addition Findon et al (1993) have shown that the particle size of the chitosan does not effect the absorption of ionic copper. However, in this study the particle size affected recovery. The finer the milled particle, the more prone it was to forming a gel and interfering with efforts to recover the copper. Increasing temperature will reduce the ability of the chitosan to absorb ionic copper. In the tests run by Findon et al (1993) and McKay et al (1989) increasing the temperature from 20°C to 30°C reduced the absorption capability of the chitosan by about 10%. Deans and Dixon (1992) showed that the best polymer for absorbing ionic copper in a concentration of $1mgl^{-1}$ or less was chitosan. In this study, it was found that contact time between the ionic copper and the chitosan was important. Improving on this raw chitosan (flake) would involve producing the chitosan as a porous resin (Kawamura et al 1993).

Chitosan was studied for uptake and release of the Cu(II) ion in distilled water (0 ppt) and artificial seawater(35 ppt). Figure 17 represents the results of adding 1g of chitosan to a solution containing $1mgl^{-1}$ of Cu(II). There is a rapid uptake of the Cu(II) by the chitosan in the first 30 minutes for both seawater and de-ionized water. The different rate of uptake between the two solutions apparently reflects the difference in pH between artificial seawater (7.6) and de-ionized water (6.5).
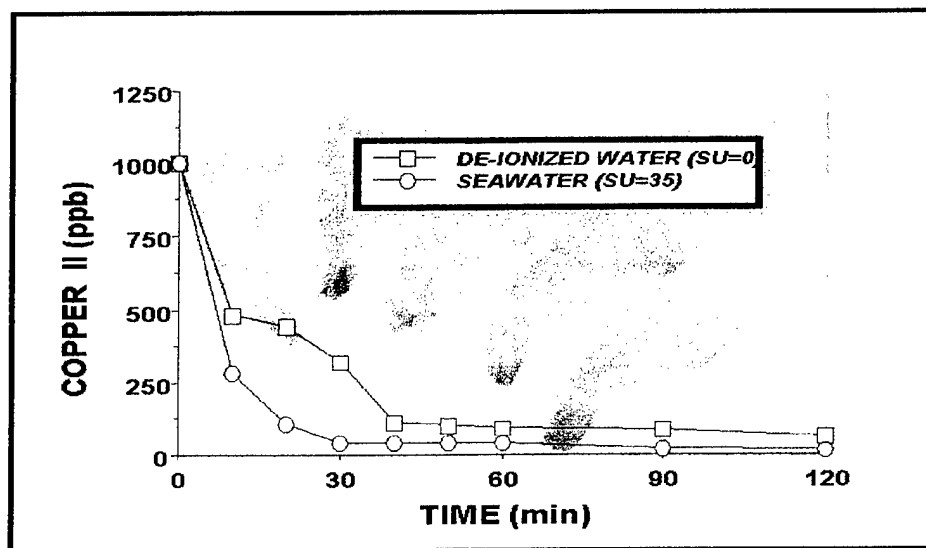

Figure 17. Loss of Cu(II) in 2 types of water with the addition of 1g of Chitosan. SU=salinity units=ppt(parts per thousand).

Figure 18 represents the loss of the Cu(II) ion from artificial seawater over the time period of the experiment. It appears that 98% of the Cu(II) is lost in the first 30 minutes. This leaves about 20ppb of Cu(II). It takes about 1 additional hour to remove 95% of the remaining Cu(II) contaminant thus reducing the potential toxicity levels to background.
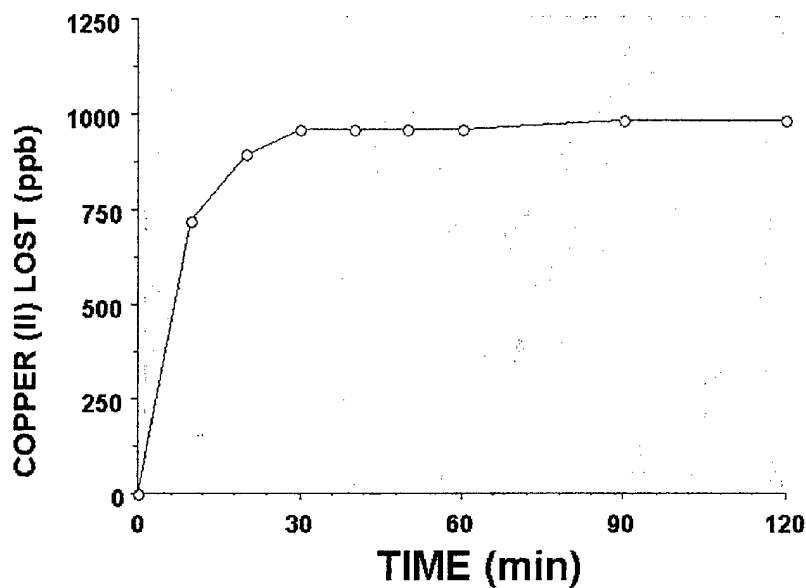
Figure 18. Reduction of Cu(II) in artificial seawater (35ppt) with 1 gram of chitosan.

Figure 19 reveals a similar pattern for loss of Cu(II) in distilled water. The exception is that after 30 minutes only 65% of the Cu(II) is absorbed. At the end of the test period there is still about 50ppb of Cu(II) left. This is indicates the ability of the seawater to enhance the complexation of the Cu(II) with chitosan.
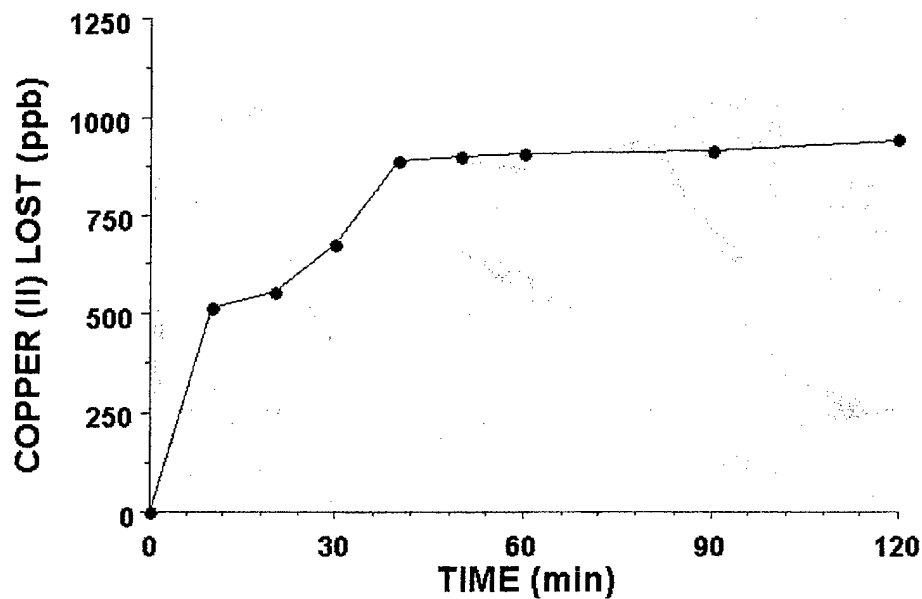

Figure 19. Reduction of Cu(II) in distilled water (0ppt) with 1 gram of chitosan.

III-B. Recovery Systems

To develop a workable cleaning system using chitosan, it is necessary to have some type of collection and recovery process. The following are suggestions on how a collection and recovery system could be developed for removal of ionic copper. Figure 20 is a hypothetical model of how a shipyard could develop a collection mechanism for their copper containing wastes. This system could be made portable by mounting it on a trailer and temporarily positioning it at the site where cleaning is progressing. The simple chitosan filter system shown in Figure 20 could be developed as a fluidized bed reactor (Figure 21), or a batch collector (Figure 22). If the chitosan filter system in Figure 20 is left just as a filter system, then it will be necessary to collect the copper contaminated chitosan and dispose of it, or dissolve it to recover the copper. In all instances, it is possible to improve water quality and reduce a waste stream.
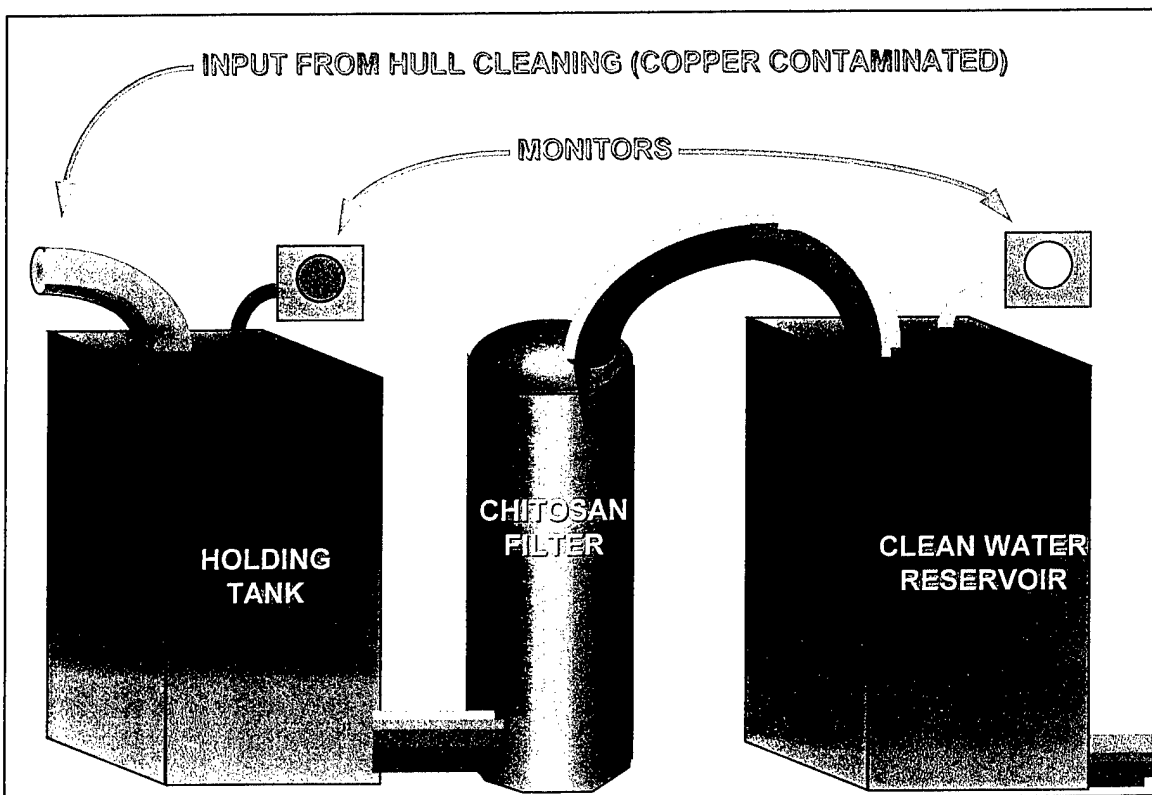

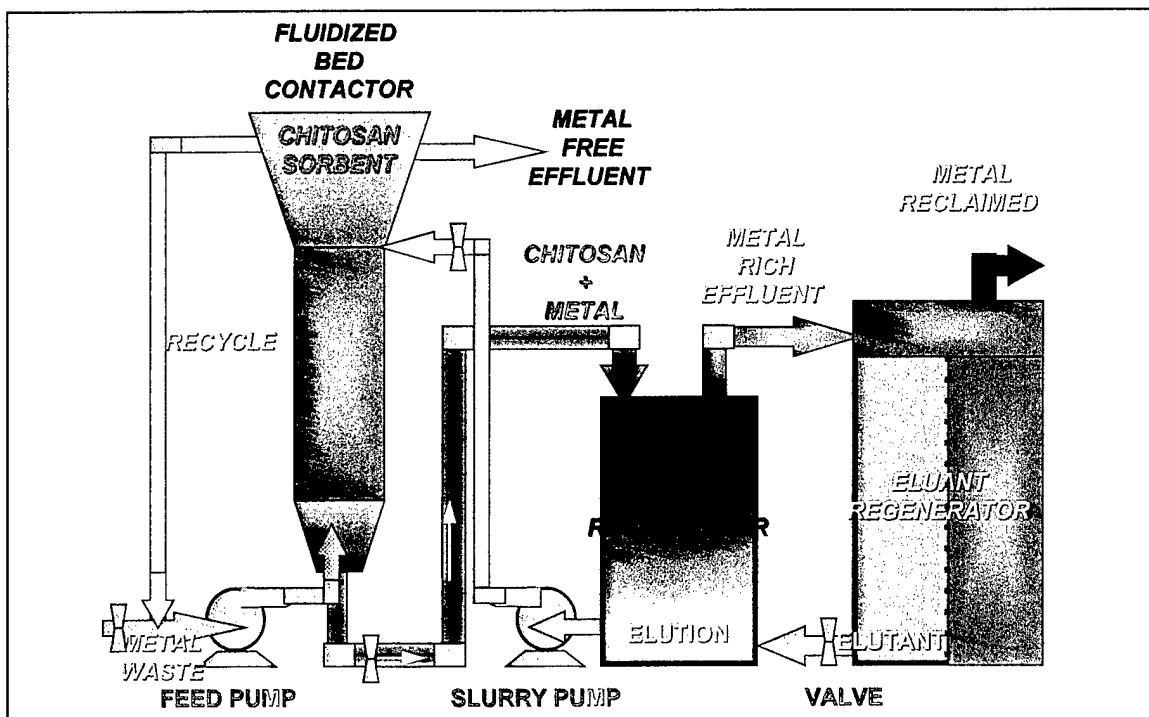**Figure 20.** Conceptual model of a waste copper handling facility.

Figure 21. Conceptual model of a fluidized bed reactor for cleaning and recycling copper contaminated water.
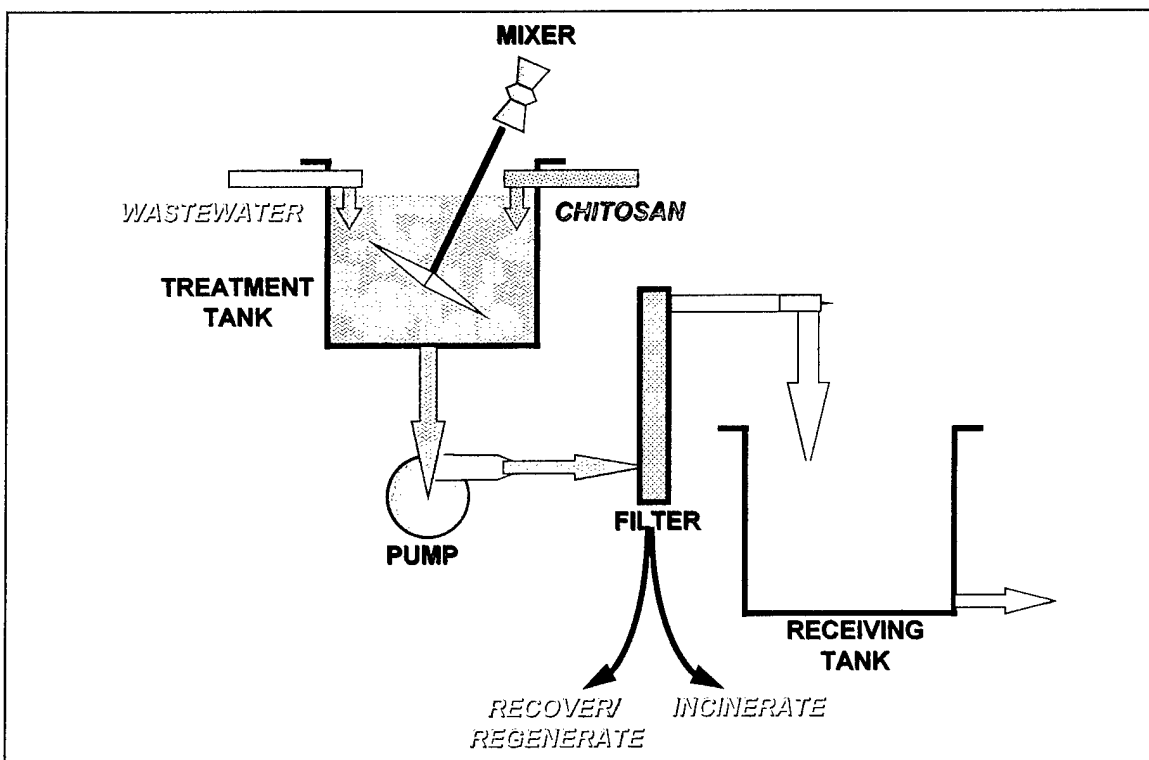

Figure 22. Conceptual model of a batch processor for cleaning and recycling copper contaminated water.

There appears to be a reasonable removal system for ionic copper from the marine environment using waste from the seafood industry. Figures 20-22 are a suggestions on how this may be possible.

IV. CONCLUSIONS

Ionic copper leached from anti-fouling coatings and concentrated in an area like a shipyard can develop toxic levels for the marine biota. Chitosan, a polyglucosamine derivative of chitin, can help remove potentially toxic levels of the ionic copper. Therefore, chitosan can
- absorb ionic copper;
- be developed from seafood waste through a relatively simple chemical process;
- be reused after recovery of the copper contamination, and
- not harm the marine environment as it is a naturally occurring compound.

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VI. ACKNOWLEDGEMENT